Non-destructive Identification and Mixture Ratio Analysis of Cotton-Polyester Blended Textile Products by IR Spectroscopy

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Abstract

Modern textiles often contain cotton-polyester products which must undergo quality assurance processes. The ability to identify the mixture ratio analysis of these products for the manufacturer is a great advantage. Preferably these methods should be non-destructive and calculated quickly. Infrared spectroscopy was used to identify textile products by absorption and soft independent modeling of class analogy. Mixture ratio analysis was conducted by analysis of the absorption spectrum and partial least squares regression. The accuracy of mixture ratio analysis has reached 2.4 %.

Keywords

IR Spectroscopy; Non-destructive Measurement, Identification and Mixture Ratio Analysis; Cotton-Polyester Textile, SIMCA, PLSR

Introduction

Cotton, a plant fiber that has been used by humans for 5000 years, is derived from a plant of the Mallow Gojibiumu genus. Cotton fibers have a hollow structure with a hole in the center called a "lumen". Microfibrils wind around the lumen in a spiral structure. The main component of the microfibril is cellulose. Cotton has the following features due to this structure;

- excellent heat retention and water absorption
- have a pleasant feel
- the fibers are prone to shrinkage, and tend to wrinkle

Cotton is a preferred textile product by these qualities.

Polyester is a chemical fiber, and a polymer based on the ester bond developed by Dickson and Whinfield in the UK in 1941, holding strength inferior only to nylon. Polyester also has excellent abrasion resistance and durability. In contrast to cotton it has the following characteristics;

- high elasticity and resistance to wrinkles
- it resists insects, mould and chemical attack
- the moisture absorption is low, and it is easy to dry
- deterioration is slow

Cotton and polyester are often blended because their characteristics complement each other. Cotton-polyester blended yarn is used in many products for shirts, work clothes, and bedding. When a product enters into market, the quality of that product must be guaranteed. Therefore, the composition ratio of the textile product must be measured. The identification and mixture ratio analysis of blended yarn products mainly involves solubility tests and release methods. These tests destroying the product, require long times, and complicated pre-treatments are necessary. Therefore, how these tests can be easily conducted is desired to be measured.

We have focused on the widely used cotton-polyester blended textile product. A non-destructive identification and mixture ratio analysis of cotton-polyester blended textile is described using infrared spectroscopy (Dozono et all., 2011, Dozono et all., Sep, 2011).

Method Development

Measurement System

When the fiber product is identified, the product that should be destroyed is the key. The identified product is used desirable. Therefore, the composition of textile products should be measured by what it is not scratch. Mid-infrared light cannot scratch the sample. The infrared absorption spectrum has composition ingredient information of the product. In addition, absorption spectrum has the quantitative information

of product. The composition of the product is identified by examining the shape of the spectrum (Koyama et all., Oct, 2011), and the blending rate of the product is analysed based on this information (Clark and Hickie, 1975, Tokutake et all., 2010).
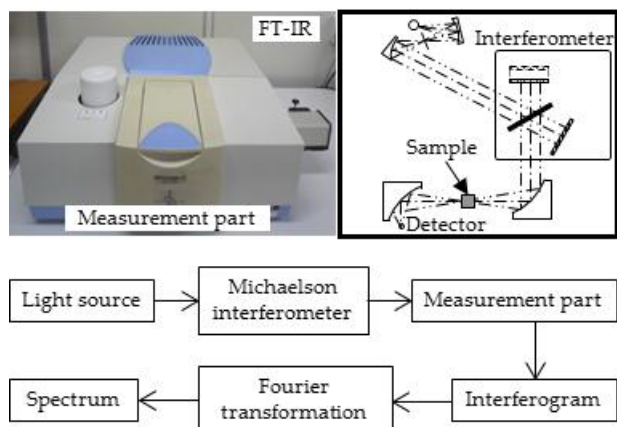

FIG. 1 MEASUREMENT SYSTEM

FIG. 2 DIFFUSE REFLECTION ATTACHMENT

The measurement system is shown in Figure 1. A Fourier transformation infrared spectrophotometer (IRPrestige, Shimadzu Co., JPN.) was used. In the measurement part, a diffuse reflectance attachment (UP-IR, Pike Tech. Co., USA.) was used. Details of this diffuse reflection attachment are shown in Figure 2. A diffuse reflectance attachment consisted of a hemisphere mirror and four reflecting mirrors. A hole with a diameter of 20 mm open to the upper semicircle mirror, was covered by the fabric sample. A reflecting mirror was placed above the fabric sample. Infrared interference light irradiated the sample from the hemispherical mirror. Thus the infrared interference light repeated the diffusion and reflection and transmission through the sample.

Soft Independent Modeling of Class Analogy (SIMCA)

SIMCA (Pirouette, GL Sciences Inc., JPN.) is a pattern analysis method (Arroio et all., 2009, Bylesjo et all., 2006, Wold, 1976, Wold and Sjöstromö, 1977), used for textile product identification. The class of the sample is

built from the absorption spectrum of the sample (Stumpe et all., 2012). These classes built by principal component analysis of each component have an individual principal component model, then used as the training sets for SIMCA. Unknown samples are tested against the training set and assigned to a class.

Unknown samples can be identified by one of three properties by SIMCA.

- Absorbance and wavenumber range of the absorption peak of the cotton-specific
- Absorbance and wavenumber range of the absorption peak of the polyester-specific
- Absorbance and wavenumber range of the absorption peak changing with the change in the blended rate

Three classes, including cotton, cotton polyester blend, and polyester have been established. Unknown samples were applied to the training set, and using the above method, the textile product could be identified.

Partial Least Squares Regression (PLSR)

PLSR (IRsolution, Shimadzu co., JPN.) is used in the mixture ratio analysis of blended samples. Absorption spectra of the samples are used as the explanatory variable. The mixture ratio of each sample is the objective variable. The principal components are extracted from the objective variable and the explanatory variables. A regression equation is created from the main components. A new objective variable is calculated from this regression equation. Next, a similar calculation using the new objective variable and explanatory variable, with an added PLS factor, is used to recalculate the objective variable. As the number of PLS factors increases, the standard error of the calibration (SEC) is smaller.

However, as the number of factors oncreases as well, Standard Error of Prediction (SEP) applied increases (Over Fitting). Therefore, the optimal number of PLS factors is validated by Leave-one-out method. When the objective variables is calculated by adding a new PLS factor, if the residual is significant before and after, the PLS factor is added. If the residual is not significant before and after, the model built before is selected (Aishima, 1992, Haaland and Thomas, 1998, Wold et all., 1984, Wold et all., 2001).

Experimental Method and Samples

Commercial textile products were regarded as samples. There 35 examples of 100 % cotton, 70

examples of cotton-polyester blended, and 35 examples of 100 % polyester. The mixture ratio and the composition of these samples have been confirmed by the JIS standard test. The sample size was 100 mm × 100 mm. The sample was measured five times to reduce the measurement error in the pattern shown in Figure 3, and the spectra were averaged. In the training set, there were 25 samples of 100% cotton and 25 of 100% polyester, and 50 blended samples. The remaining samples (100% cotton: 10, cotton-polyester blended: 25, 100% polyester: 10) were used for validation.
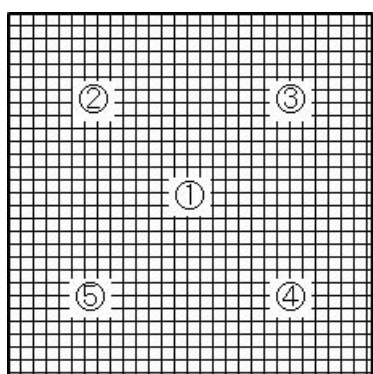

FIG. 3 PLACEMENT OF MEASUREMENTS ON EACH SAMPLE

Spectra were measured over the range of 4000–700 cm^{-1}, at a resolution of 4 cm^{-1}, and integrating times of 20 times. Absorption spectrum measurements thus took about 60 s.

Experimental Result

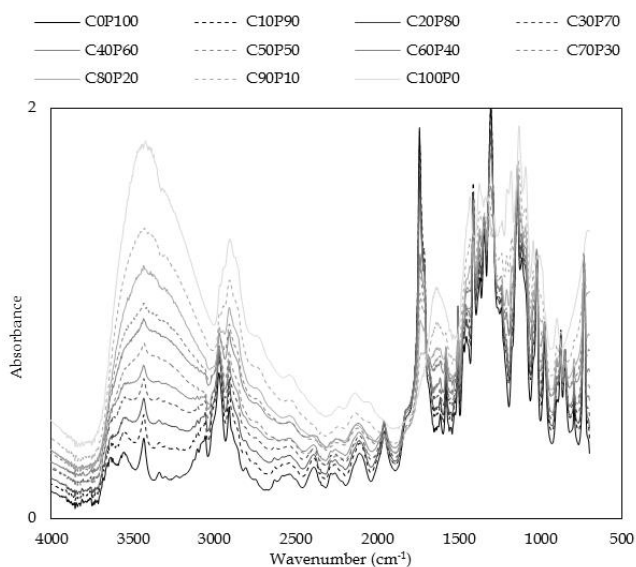### Absorption Spectra of Each Mixture Ratio

FIG. 4 ABSORPTION SPECTRA OF THE BLENDED YARNS

The infrared absorption spectra of the blended yarns are shown in Figure 4, in which "C" indicates the percentage of cotton, and "P" indicates the percentage of polyester (C100P0: 100 % cotton, C90P10: 90 % cotton and 10 % polyester blended, and C0P100: 100 % polyester). These infrared absorption spectra change the percentage of mixing of the cotton and polyester in increments of 10%.

Figure 4 shows that each cotton or polyester textile product has a characteristic absorption profile. Each absorbance varies depending on the ratio of cotton and polyester. The assignment of the absorption peaks to polyester or cotton is shown in Table 1 (Chung et all., 2004, Okuyama and Mitsu, 1999, Wang et all., 2006). For example, in the cotton spectrum, absorbance in the 3600–3200 cm^{-1} region, due to the OH stretch vibration, increases as the ratio of cotton increases

(Allen et all., 2007). In polyester spectrum, the overtone absorption peak at 3435 cm^{-1} from the C=O stretching vibration overlaps with the OH stretch vibration of the cotton spectrum. This absorption peak appears when the amount of cotton is small. The absorption peak assigned to the C=O stretching vibration of the polyester at 1740 cm^{-1} is always strong. The intensity of this absorption peak is proportional to the amount of polyester.

However, at some places in the absorption spectra, the absorbance does not change. This position is called an isosbestic point, and important in analytical chemistry. The cotton-polyester continuum has several isosbestic points. Five positions in the spectra (1696, 1430, 1416, 1285 and 1140 cm^{-1}) are isosbestic points used to normalize the spectra.

Table 1 shows the characteristic peaks of cotton or polyester, as measured by infrared spectroscopy. The mixture ratio of the sample is reflected in the absorption spectrum. Therefore, by analysis in the absorption spectrum in the range including these characteristic absorption peaks, the identification and the mixture ratio analysis of cotton polyester blended sample can be made.

Identification of Textile Product by SIMCA

To measure the quality of the product, the composition should be well known. A model was built to classify cotton, polyester, and cotton-polyester blended samples, then a training set using the absorption spectrum of the samples and SIMCA. The samples used in the training set are shown in Table 2-A. The validation samples are shown in Table 2-B. The validation samples were classified by the training set.

TABLE 1 ASSIGNMENT BY ABSORPTION PEAK OF THE COTTON AND POLYESTER

Wavenumber (cm^{-1})	Assignment	Cotton	Polyester
3600-3500	OH intermolecular H-bond	○	
3500-3300	Free OH str.	○	
3435	C=O str. (Overtone)		○
3059	C-H str. (C=C-H)		○
2974	C-H str. (-CH$_2$-)	○	○
2910	C-H str. (-CH$_2$-)	○	○
1740	C=O str.		○
1713	C=O str.		○
1649	O-H	○	
1612	C=C str. (ring C=C, C=C-C=C), C=O str.		○
1577	C=C str. (ring C=C, C=C-C=C)		○
1504	Skelton (aromatic ring), C=C str.		○
1433	O-H def.	○	
1412	C-H$_2$ sci., C-H$_2$ wagg.		○
1373	C-H$_2$ sci.	○	○
1346	C-H def.		○
1303	C-O str.		○
1240	Ether R-O-R asym. str.	○	○
1207	C-O str. (alcohol C-OH)	○	
1180	C-O str.	○	○
1142	C-H def.		○
1132	C-H$_2$ wagg., C-H$_2$ twist.	○	
1115	C-H def.		○
1093	C-H$_2$ twist	○	
1045	C-H$_2$ rocking	○	○
1018	C-H def.		○
1004	C-O str. (alcohol C-OH)	○	
975	C-H bend (C=C-H)		○
898	C-H bend, C-H$_2$ rocking	○	○
873	C-H bend (ring puckering)		○
850	C-H bend (ring puckering)		○
795	C-H bend (ring puckering)		○
734	C-H$_2$ rocking		○

TABLE 2 SAMPLE DATA

(A) Calibration data.

	Number	Max (%)	Min (%)	Ave (%)
Cotton	25	Cotton 100 %		
Polyester	25	Polyester 100%		
Blended	50	98.4	8.4	47.3

(B) Validation data.

	Number	Max (%)	Min (%)	Ave (%)
Cotton	10	Cotton 100 %		
Polyester	10	Polyester 100%		
Blended	20	99.6	8.8	48.1

TABLE 3 RESULTS OF IDENTIFICATION

| Correct	No match	Missing
27/40	9/40	4/40

The results of the identification for each sample spectrum are shown in Table 3. These results use the terms "Missing" and "No match". When the model results in a "No match", it attempts to reanalyze the sample. However, the "Missing" result is a mis-classification. The result of "Missing" must be zero.

The method of model building was improved to reduce the occurrences of "Missing" results. First, we focused on the single to noise (S/N) ratio of the absorption spectrum. Variation in the S/N ratio of the absorption spectrum results in large errors. This is a potential source of "Missing" results. The absorption spectra were reprocessed to give a consistent S/N ratio by normalization and taking the 1st or 2nd differential. The spectra were normalized at the isosbestic points. Second, we looked at the method of measuring the spectra. The two sides of the fabric are often different. Therefore the correct fabric spectrum cannot be obtained from the measurement of one side. The samples were re-measured at five points on both sides of the sample. The 10 absorption spectra were then averaged.

TABLE 4 RESULTS OF IDENTIFICATION BY THE IMPROVED MODEL

	Correct		No match		Missing	
	Face	Both	Face	Both	Face	Both
Raw	27	28	9	10	4	2
1st diff	35	32	3	7	2	1
2nd diff	25	33	5	3	10	4
1416 normal	25	30	8	9	3	1
1416+1st diff	29	36	3	4	2	0
1416+2nd diff	25	32	7	4	8	4
1285 normal	29	29	8	11	3	0
1285+1st diff	34	35	4	5	2	0
1285+2nd diff	25	32	7	3	8	5
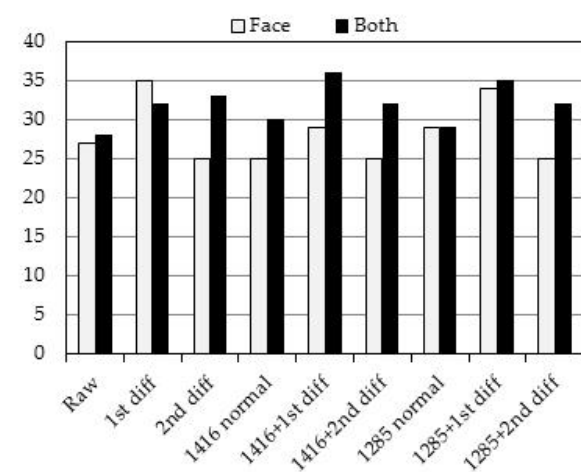
(A) Number of "Correct".
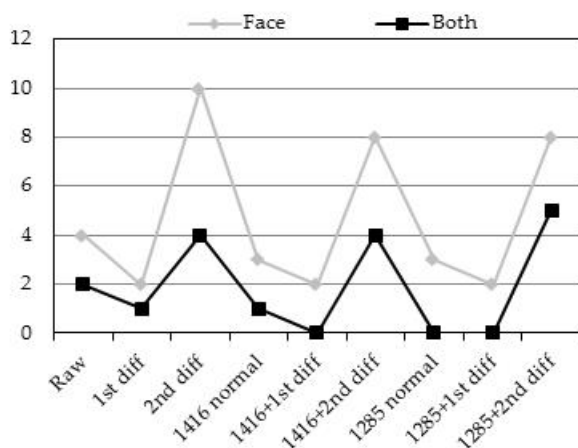
(B) Number of "Missing".

FIG. 5 VALIDATION RESULTS BY THE IMPROVED MODEL

The validation results using the improved model are shown in Table 4, and the number of "Correct" and "Missing" are shown in Figure 5. By these results, the number of correct answers when measuring both sides of the fabric has increased. This has also reduced the number of "Missing". The result by model of the both sides spectrum is better than that by model of the single side spectrum. In spectral processing, normalization is better than the result of raw data. In differential process, result of 1st differential is the best

result, which that of the 2nd differential is not good. Absorbance and the full width at half maximum of the spectrum are very small in the 2nd differential spectrum. Therefore, S/N ratio is less. Based on the above, it was considered that the result of the 2nd differential spectrum is underirable.

The best results were utilized, by employing normalization at 1416 cm^{-1} taking the 1st differential. There are no "Missing" results using this model. The spectra of polyester and cotton and the discrimination power of this model are shown in Figure 6. Discrimination power is a measure to build an identification model. From Figure 6, discrimination power at the 1740 cm^{-1} peak is high. In this range, polyester has an absorption peak which is strong shown in Table 1. To extract information from this absorption peak, variations in the S/N ratio must be low. Because the absorption spectrum has been processed by the first differential and normalization, the improved model has the required characteristics. This means that the model can now be used to discriminate among cotton, cotton-polyester blend, or polyester.
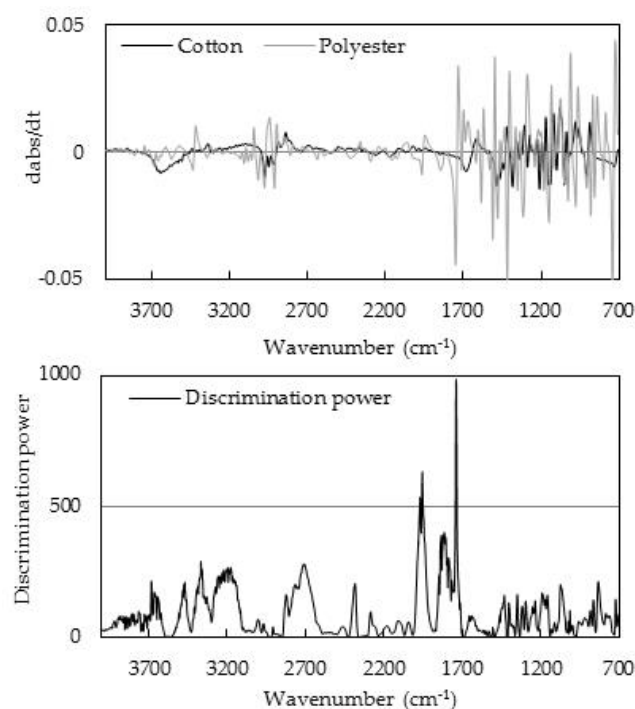

FIG. 6 SPECTRA OF COTTON AND POLYESTER, AND DISCRIMINATION POWER IN IMPROVED MODEL

Mixture Ratio Analysis by PLSR

If the unknown sample is determined to be a cotton-polyester blended textile by SIMCA, it is desirable to determine the composition of this textile (Nitta et all., 2004). The mixture ratio of blended textile was analysed by PLSR. The same blended textiles as Table

2 were used as the samples. The calibration curve was built using PLSR of 50 samples. The method was validated by fitting 20 samples of cotton polyester blend textile to the calibration curve (Koyama et all., Sep, 2011). To reduce measurement errors, the absorption spectrum was processed by taking the 1st differential and normalization, as in identification analysis; then the errors in the calibration curve were evaluated.

Table 5 shows the results of several processes on the data used to develop the calibration curve. The number of PLS factor in calibration curves in Table 5 is 3. The SEC of the calibration curve for the data including measurement of both sides is the smallest.

TABLE 5 DATA FOR THE CALIBRATION CURVE AFTER PROCESSING

	R		SEC (%)	
	Face	Ave	Face	Ave
Raw	0.959	0.975	6.9	5.4
1st diff	0.967	0.984	6.2	4.3
2nd diff	0.965	0.983	6.3	4.4
1416 normal	0.969	0.982	5.9	4.6
1416+1st diff	0.976	0.988	5.3	3.7
1416+2nd diff	0.974	0.986	5.4	4.1
1285 normal	0.974	0.977	5.4	5.2
1285+1st diff	0.964	0.985	9.4	4.2
1285+2nd diff	0.962	0.982	6.6	4.6

TABLE 6 DATA FOR THE VALIDATION RESULTS

	Factor		SEP (%)	
	Face	Ave	Face	Ave
Raw	5	10	5.9	2.7
1st diff	6	5	6.3	4.2
2nd diff	5	2	4.3	5.0
1416 normal	5	6	5.0	2.4
1416+1st diff	6	5	6.0	2.4
1416+2nd diff	5	4	7.8	3.7
1285 normal	5	8	5.8	2.7
1285+1st diff	6	5	5.9	3.2
1285+2nd diff	7	4	4.8	4.2

The SEC of the calibration curve for the normalized data is less than that of the raw data. In addition, taking the 1st differential improves the results. These results have the same trends as the identification analysis by SIMCA.

We proceeded with the methods that had the best results from Table 5. The conditions were; to measure the IR spectrum of both sides of the textile, to normalize the 1416 cm^{-1} peak, and take the first differential. Table 6 shows results of calculation from the calibration curve in each condition. The calibration curve for the optimum number of PLS factors in these conditions is shown in Figure 7 in which the optimum

number of PLS factors is 5, giving a correlation coefficient of 0.994, and an SEC of 2.7%. 20 samples are verified by using this calibration curve. The validation result based on this calibration curve is shown in Figure 8. The SEP of the validation results is 2.4%. The fiber mixture in the product is displayed in increments of 5%. The fiber mixture measurement method based on this calibration curve can be used at this level of accuracy, because the SEP is less than 5%. These results show that a method has been developed which is able to analyze the mixture ratio of cotton-polyester blended products using PLSR and absorption spectra.
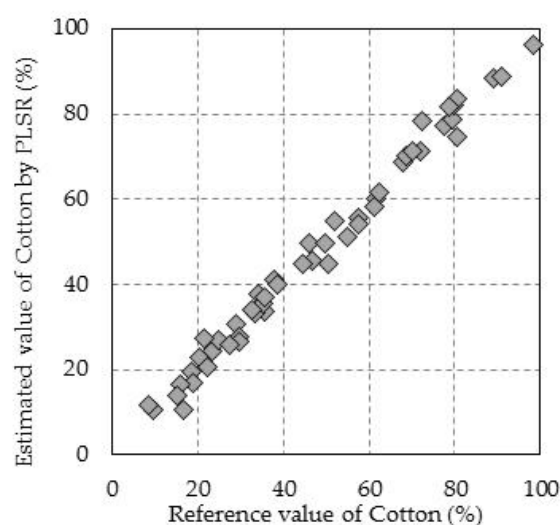

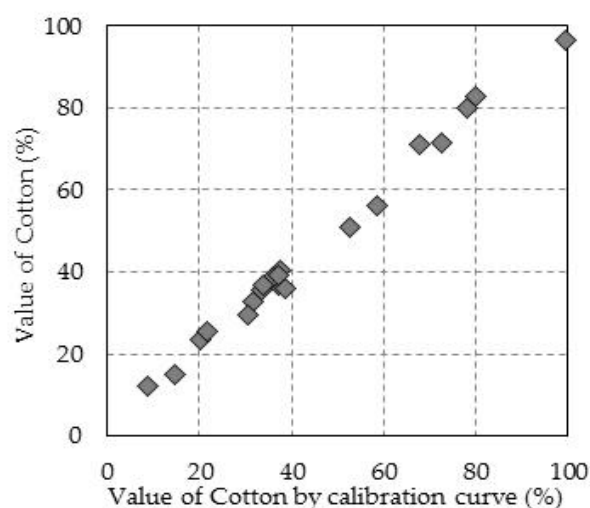FIG. 7 CALIBRATION CURVE FOR THE OPTIMUM NUMBER OF PLS FACTORS

FIG. 8 VALIDATION RESULTS

Conclusion

The identification and mixture ratio of cotton, polyester, and cotton-polyester blended textiles have been analysed using infrared spectroscopy, then errorless identification (no misidentified samples)

model has been built using SIMCA. To analyze the mixture ratio, a calibration curve has been built that can evaluate the ratio to an accuracy of 2.4%. It has been confirmed better to measure both sides of the sample. In addition, the results were improved by applying 1st differential processing and normalization to the absorption spectra.

This method can measure samples in a non-destructive way. The averaged spectra require 10 minutes to obtain. This is short compared with other evaluation methods. It is also simple, based on diffuse reflection FT-IR. As a simple and effective method it can be used as an identification and mixture ratio analysis method for cotton and polyester textiles.

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